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# PATENT SPECIFICATION

(11) 1 568 699

(21) Application No. 46624/76 (22) Filed 9 Nov. 1976
(31) Convention Application No. 630428
(32) Filed 10 Nov. 1975 in
(33) United States of America (US)
(44) Complete Specification published 4 June 1980
(51) INT CL³ G09F 3/02 B32B 3/00
(52) Index at acceptance
B8F BF BG

(19)

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## (54) IMPROVED COLOR-CODED IDENTIFIER MICROPARTICLES

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 3 M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is performed, to be particularly described in and by the following statement:—

This invention relates to color-coded microparticles and their manufacture. These microparticles are useful in tagging substances for the purposes of retrospective identification of the substance.

The use of microparticles bearing coded information to tag substances for the purpose of retrospective identification is known. U.S. Patents 3,772,200 and 3,897,284 describe microspheres containing trace elements in various combinations and concentrations constituting identifying codes. Decoding entails the use of sophisticated analytical instruments such as an electron microprobe analyzer.

More convenient decoding is possible by using color-coded identifier microparticles wherein the identifying code is provided by sequential arrangement of visually distinguishable colors. The code can be read with an inexpensive microscope or magnifying glass. Color-coded identifier microparticles of this type are described in U.S. patent specification No. 4,053,433. These microparticles are primarily of uniform geometric shape, normally being either spherical, cylindrical or rectangular. Processes disclosed in the application for producing these microparticles are inherently rather expensive.

The present invention provides color-coded identifier microparticles which can be economical to manufacture.

According to the present invention there is provided a microparticle useful for tagging a substance to permit retrospective identification, the microparticle being encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers, the distance across the color sequence measuring 15 to 1,000 micrometers, the external surfaces of the colored layers at the extremities of the code being generally flat and parallel to each other whilst the other surfaces of the microparticle have irregular, broken shapes, and the broadest dimension of the particle being greater than the distance between said parallel surfaces. These microparticles differ from those described in Specification No. 4053433 by their novel geometric configuration. That is, the external surfaces of the code of each microparticle are generally flat and parallel to each other and its surfaces have irregular, broken shapes.

The invention also provides a batch of microparticles useful for tagging a substance to permit retrospective identification, the microparticles being uniformly encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers and each microparticle measuring 15 to 1,000 micrometers across the color sequence, the external surfaces of the colored layers at the extremities of the code of each microparticle being generally flat and parallel to each other whilst its other surfaces have irregular, broken shapes, and for most of the microparticles the broadest dimension of the microparticle being greater than the distance between its said parallel surfaces; and a plurality of batches of microparticles useful for tagging substances to permit retrospective identification, the microparticles of each batch being uniformly and uniquely encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers, the distance across the color sequence measuring 15 to 1,000 micrometers, the external surfaces of the colored layers at the extremities of the code of each microparticle being generally flat and parallel to each other whilst its other surfaces have irregular, broken shapes, and for most of the microparticles the broadest

dimension of the microparticle being greater than the distance between its said parallel surfaces.

The invention further provides a process for preparing irregularly-shaped, color coded identifier particles which comprises combining at least three visually distinguishable colored layers in a predetermined color sequence to form a laminate having a thickness of 15 to 1,000 micrometers, and randomly breaking up the laminate into microparticles encoded by an orderly sequential arrangement of colored layers so that the external surfaces of the colored layers at the extremities of the code of each microparticle are generally flat and parallel to each other and its other surfaces have irregular, broken shapes, the broadest dimension of most of the particles being greater than the distance between said parallel surfaces.

In a preferred embodiment of the process of the invention, the colored layers are individually deposited in liquid form upon a releasable carrier sheet and sequentially hardened or dried to a solid state to provide a laminate which is removed from the carrier sheet and then comminuted into microparticles. Alternatively, pre-formed colored layers, such as may be individually formed by extrusion, are combined into a laminate as, for example, in a heated platen press.

A wide variety of materials may be used to form the colored layers of the microparticles. The preferred materials are rapid-curing organic resins which when cured are brittle at room temperature. Melamine resins such as melamine alkyds and melamine acrylates are especially preferred.

Organic resins which form sheets which are brittle only when cooled, such as cellulose acetate butyrate or polyethylene, may also be used to form the colored layers of the microparticles. However, the cost of cooling such materials during comminution may limit their utility.

Inorganic materials such as sodium silicate are also useful.

The color of each layer is generally provided by the addition of dye or pigment prior to forming the layer. Clear or colorless layers may also form part of the identifying code. Pigments producing opaque colored layers are preferred over dyes which tend to produce transparent layers. The demarcation between layers is less apparent when the layers transmit light. Dyes, when added to a white pigment such as titanium dioxide, produce desirably opaque colors.

In addition to using colors which are responsive to visual light, fluorescent and phosphorescent materials which are responsive to ultraviolet light may be incorporated into the code and may provide an additional function. For example, an explosive may be tagged with microparticles having a fluorescent color on one of the outermost segments. After detonation, the blast debris may be illuminated with an ultraviolet light source to provide a quick indication, e.g., that the explosive was or was not manufactured in accordance with specific government regulations, namely permissible or non-permissible explosives. Upon retrieval of the microparticles the color code may be read to ascertain such information as manufacturer and lot number.

It is preferred in some cases to incorporate magnetic material into one or more layers of the microparticles. This is particularly desirable when bulk materials or explosives are tagged. Retrieval of magnetic microparticles is enhanced by the use of a magnet.

Magnetic material may be heavily concentrated in a single layer, in which case the color of the magnetic material may determine the color of the layer. Alternatively, a small amount of magnetic material may be incorporated into each layer without significantly affecting the color of individual layers. Generally, the magnetic material may be added in an amount of up to one-half the weight of the pigment or dye without masking the color of the layer.

When using liquids to create the laminate from which the novel microparticles are broken, it is preferred to harden or cure each layer partially before the next layer is applied. This prevents the fresh layer from attacking the underlying layer to cause the colors to run together. The laminate is generally completely hardened or cured prior to being broken up into microparticles.

Using conventional coating techniques, the preferred thickness of each layer is about 5 to 50 micrometers. Layers thicker than 5 micrometers are generally easy to read without a high degree of magnification. Layers thicker than 50 micrometers simply result in economic waste. The number of layers in each code may range from a minimum of three to a maximum number which is limited only by the overall size requirements of the microparticles. Microparticles greater than 1000 micrometers at their broadest dimension tend to be noticeable to the naked eye, and as a result, their utility for most tagging purposes is limited.

In order to ensure that a microparticle having a complete code is retrieved and identified, it is desirable to tag articles or substances which must be distinguished from each other with microparticles having

the same number of layers. For example, explosives may be uniformly tagged with six-layered microparticles, each having a magnetic layer as one of the outermost layers of the particle. When a microparticle is retrieved from the blast debris, the number of layers can be counted. If less than six layers are present the microparticle should be discarded as being incomplete and a microparticle bearing a complete code selected.

In the laboratory, fragmentation of the laminate is most effectively accomplished by using a high speed blender with air suspension of the laminate. It has also been found that liquid suspension of the laminate during the fragmentation step results in the formation of a greater proportion of microparticles in the desired size range. However, the addition of a liquid tends to increase the overally cost of manufacture.

A ball mill may also be used to break up the laminate. However, a larger proportion of incomplete codes is produced by this method.

Prior to size classification of the fragmented material, it may be washed and dried. During the washing step some of the undersized (dust) particles are suspended and removed by decantation. The remaining material may be classified by screening or sieving and divided into three groups: (a) Particles whose largest dimension is greater than four times the distance between the outer surfaces of the two outer code layers. These should be further fragmented. (b) Particles whose largest dimension is from one to four times the distance between the outer surfaces of the two outer code layers. Most of these include the full code and are preferred for tagging. (c) Particles whose largest dimension is less than the length of the color code. These should be discarded.

It has been found that the microparticles of the invention are particularly useful for tagging art objects, bonds, certificates and similar items where counterfeiting is a problem. For this purpose the microparticles may be incorporated into a clear lacquer which is applied to an inconspicuous place on the object.

When tagging liquid substances, the density of the microparticles should approximate the density of the liquid in order to maintain them in suspension. The density of the microparticles may be controlled by well known means such as by incorporating glass bubbles to form colored isotactic foam layers.

To provide a secondary means of identification, and additional coded information, coded microparticles such as those described in U.S. Patent 3,772,200 may be incorporated into one or more colored layers. This would inhibit counterfeiting of the color-coded microparticles themselves. Additionally, it may be desirable to tag a substance with microparticles bearing different codes. For example, two-layered microparticles may be included along with three-layered microparticles. In that case both types of microparticles must be isolated and read.

In the accompanying drawings Figures 1 to 3 are perspective views of three identifier microparticles of the invention.

In Figure 1 microparticle 10 consists of six colored layers 12 in a preselected color sequence to constitute an identifying code. The external surfaces 14 and 16 of the colored segments are parallel to each other. The other surfaces of the particle have irregular, broken shapes. The broadest dimension of the particle lies across surfaces 14 and 16, and this dimension is greater than the distance between the parallel surfaces.

In Figure 2 microparticle 20 shows that highly irregular shapes may be useful in the invention.

In Figure 3 microparticle 30 has magnetic material incorporated into the colored layers 32. The particle is shown oriented on a piece of paper with a magnetic so position below the paper that its lines of magnetic flux are perpendicular to the paper. This causes the particle to stand on edge so that the color sequence can be easily read.

The following non-limiting examples further illustrate the invention:

## EXAMPLE 1

Microparticles were formed from melamine alkyd resin wherein one of the outermost colored segments of the code is fluorescent red and the other contains magnetic material.

A resin base was prepared by mixing together 25 grams of a 50 percent solids soya alkyd resin in xylene, 25 grams of a 55 percent solids alkylated melamine in butanol and xylene, and 0.5 g of 20 percent para-toluene sulfonic acid in isopropanol.

The following four coating mixtures were each prepared by adding to 50.5 g of resin base the following additives:

| Coating Mixture | Additive | Amount |
|---|---|---|
| A | Fluorescent Red dye in polysulfonamide resin | 8.5 g |
| B | Rutile titanium dioxide pigment | 9.0 g |
| C | Quinacridone red dye | 3.0 g |
| | Red iron oxide pigment | 2.0 g |
| D | Carbonyl iron powder | 6.7 g |
| | Colloidal silica | 1.0 g |

Th se coating mixtures were coated n a polyester carrier film (.002 in., 50.8 microm ters) with a wire wound rod in the sequence shown below.

| Coat | A | B | C | B | C | B | D |
|---|---|---|---|---|---|---|---|
| Dry thickness (mils) | .8 | .3 | .2 | .3 | .2 | .3 | 1.5 |
| (Micrometers) | (20.3) | (7.6) | (5.1) | (7.6) | (5.1) | (7.6) | (38.1) |

The thickness of the seven combined layers was .0036 inch, (91.4 micrometers). After each layer was applied it was heated for 15 seconds at 140°C. After the last layer was applied the laminate was heated at 140°C for 10 minutes to obtain a full cure of the alkyd-melamine resin.

The laminate was placed in a dry blender which was operated for about 20 seconds.

EXAMPLE 2

Microparticles of sodium silicate were prepared from the following three coating mixtures:

| Coating Mixture | Ingredients | Amount |
|---|---|---|
| A | Sodium Silicate | 70 g |
| | Blue pigment | 7 g |
| | Water | 3 g |
| B | Sodium Silicate | 70 g |
| | White pigment (Titanium dioxide) | 7 g |
| | Water | 4 g |
| C | Sodium Silicate | 70 g |
| | Carbonyl iron | 30 g |

The coating mixtures were applied to a .001 inch (about 25.4 microns) aluminized polyester carrier film with a wire wound rod in the following sequence:

B—A—B—A—B—A—C.

The layers were placed on the aluminized side of the carrier film to prevent beading of the first layer. Each layer was allowed to dry in an oven for a few seconds at 70°C before the next coat was applied.

After the last layer was applied a piece of the laminate was dried for a few minutes at 70°C and then removed from the carrier film by flexing the polyester sharply. The laminate, which was white on one side and black on the other side, was still somewhat flexible. It was dried at 100°C for a few minutes to make it brittle, at which point it was easily broken into microparticles by a blender as described in Example 1.

Another piece of the laminate was dried for about 10 minutes at 100°C. The laminate became very brittle. The laminate was then removed by flexing the polyester sharply. In this case the aluminum from the carrier film vapor coat adhered to the laminate so that the microparticles were black on one side and had an aluminum mirror on the other side. When the microparticles were viewed on edge, the colored layers were seen easily, but the aluminum was too thin to be seen edgewise at 100× magnification. Nevertheless, because it could be seen from the side, it might be considered as part of the code.

When the microparticles are immersed in water, they tend to re-dissolve within a few hours. They can be made insoluble by immersion in a solution of a metal salt which will replace the sodium in the sodium silicate with a metal whose silicate is insoluble in water. For example, immersion of the particles for 24 hours in a 20 percent aqueous solution of aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) will make the particles insoluble in water of pH 8.

WHAT WE CLAIM IS:—

1. A microparticle useful for tagging a substance to permit retrospective identification, the microparticle being encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers, the distance across the color sequence measuring 15 to 1,000 micrometers, the external surfaces of the colored layers at the extremities of the code being generally flat and parallel to each other whilst the other surfaces of the microparticle have irregular, broken shapes, and the broadest dimension of the particle being greater than the distance between said parallel surfaces.

2. A microparticle according to Claim 1 wherein magnetic material is incorporated into one or more of the colored layers.

3. A microparticle according to Claim 1 or 2 wherein trace-element-encoded microparticles are incorporated into one or more of the colored layers to provide a secondary means of identification.

4. A microparticle according to Claim 1, 2 or 3 wherein at least one of the colored layers contains a fluorescent or phosphorescent material.

5. A microparticle according to any preceding claim wherein the colored layers are formed from an organic resin which is brittle at room temperature when fully cured.

6. A microparticle according to Claim 5 wherein the colored layers are formed from melamine alkyd or melamine acrylate resin.

7. A batch of microparticles useful for tagging a substance to permit retrospective identification, the microparticles being uniformly encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers and each microparticle measuring 15 to 1,000 micrometers across the color sequence, the external surfaces of the colored layers at the extremities of the code of each microparticle being generally flat and parallel to each other whilst its other surfaces have irregular, broken shapes, and for most of the microparticles the broadest dimension of the microparticle being greater than the distance between its said parallel surfaces.

8. A batch of microparticles according to Claim 7 wherein magnetic material is incorporated into one or more of the colored layers.

9. A batch of microparticles according to Claim 7 or 8 wherein trace-element-encoded microparticles are incorporated into one or more of the colored layers to provide a secondary means of identification.

10. A batch of microparticles according to Claim 7, 8 or 9 wherein at least one of the colored layers contains a fluorescent or phosphorescent material.

11. A batch of microparticles according to any of Claims 7 to 10 wherein the colored layers are formed from an organic resin which is brittle at room temperature when fully cured.

12. A batch of microparticles according to Claim 11 wherein the colored layers are formed from melamine alkyd or melamine acrylate resin.

13. A plurality of batches of microparticles useful for tagging substances to permit retrospective identification, the microparticles of each batch being uniformly and uniquely encoded with an orderly sequential arrangement of at least three visually distinguishable colored layers, the distance across the color sequence measuring 15 to 1,000 micrometers, the external surfaces of the colored layers at the extremities of the code of each microparticle being generally flat and parallel to each other whilst its other surfaces have irregular, broken shapes, and for most of the microparticles the broadest dimension of the microparticle being greater than the distance between its said parallel surfaces.

14. Microparticle batches according to Claim 1 wherein magnetic material is incorporated into one or more of the colored layers of at least one batch.

15. Microparticle batches according to Claim 13 or 14 wherein trace-element-encoded microparticles are incorporated into one or more of the colored layers of at least one batch to provide a secondary means of identification.

16. Microparticle batches according to Claim 13, 14 or 15 where at least one of the colored layers of at least one batch contains a fluorescent or phosphorescent material.

17. Microparticle batches according to any of Claims 13 to 16 wherein the colored layers of at least one batch are formed from an organic resin which is brittle at room temperature when fully cured.

18. Microparticle batches according to Claim 17 wherein the said colored layers are formed from melamine alkyd or melamine acrylate resin.

19. A process for preparing irregularly-shaped, color coded identifier particles which comprises combining at least three visually distinguishable colored layers in a predetermined color sequence to form a laminate having a thickness of 15 to 1,000 micrometers, and randomly breaking up the laminate into microparticles encoded by an orderly sequential arrangement of colored layers so that the external surfaces of the colored layers at the extremities of the code of each microparticle are generally flat and parallel to each other and its other surfaces have irregular, broken shapes, the broadest dimension of most of the particles being greater than the distance between said parallel surfaces.

20. A process according to Claim 19 wherein the colored layers of the laminate are sequentially applied to a releasable carrier sheet and said carrier sheet is removed prior to breaking up the laminate.

21. Color-coded microparticles substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

22. Color-coded microparticles substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

23. Color-coded microparticles substantially as hereinbefore described with reference to Figure 3 of the accompanying drawings.

24. Color-coded microparticles substantially as hereinbefore described in Example 1.

25. Color-coded microparticles substantially as hereinbefore described in Example 2.

26. A process for preparing color-coded microparticles, the process being substantially as hereinbefore described in Example 1.

27. A process for preparing color-coded microparticles, the process being substantially as hereinbefore described in Example 2.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980. Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 1

FIG. 2

FIG. 3